



Microwave-activated direct synthesis of acrylonitrile from glycerol under mild conditions: Effect of niobium as dopant of the V-Sb oxide catalytic system

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ABSTRACT

Glycerol is a major by-product in biodiesel production, which raises a critical need to develop efficient valorization processes. This study shows how both conventional thermal activation and microwave irradiation are able to selectively transform glycerol into acrylonitrile, this performance is modulated by niobium doping of Sb_nV/Al_2O_3 catalysts under mild reaction conditions. To the best of our knowledge, we report the highest selectivity (83.8%) to acrylonitrile from glycerol at good conversion values (46.8%).

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1. Introduction

It has been proposed that commodity chemicals derived from fossil resources at present will be produced in future biorefineries from renewable resources, such as plant-derived sugar and other compounds [1]. Glycerol has to be one of the building blocks in the biorefinery feedstock for it is a major by-product in biodiesel production via transesterification of vegetable oils [2,3]. Many valuable chemicals can be obtained using glycerol as a feedstock [3], such as hydrogen, dihydroxyacetone, propanediols [4], acrolein [5], glycerides, or epichlorohydrin, among others.

Glycerol oxidation produces important intermediates in the synthesis of fine chemicals. Due to the high boiling point of glycerol, its selective oxidation is normally carried out in the liquid phase. The three hydroxyl groups in the glycerol molecule present similar reactivity, making it difficult to modulate the oxidation towards a primary hydroxyl group to yield glyceric acid or to a secondary alcohol function to produce dihydroxyacetone and hydroxypyruvic acid. This complex reaction network [6] limits the selectivity to desired products. In this sense, the use of an additional reactant (ammonia) to focus product distribution towards nitriles has proved to be an attractive option to modulate the selectivity, minimizing side reactions and affording high value-

added products [7,8] as acrylonitrile; which is the nitrile manufactured on the largest scale. Most industrial acrylonitrile is produced through the catalytic ammoniation of propylene, typically obtained by steam cracking or catalytic cracking of petroleum fractions at temperatures near 400 °C. Thus, this method allows obtaining acrylonitrile from a renewable feedstock, such as glycerol.

Traditionally, organic syntheses are carried out by conductive heating using an external heat source (e.g., an oil bath), which is a comparatively slow and inefficient method for transferring energy into the system. In contrast, microwave (MW) irradiation produces efficient internal heating (in-core volumetric heating) by direct coupling microwave energy with the molecules (solvents, reagents and catalysts) that are present in the reaction mixture. Thus, high-speed synthesis with microwaves has attracted much attention in recent years [9–12]. Microwave-enhanced chemistry is based on the efficient heating of materials by “microwave dielectric heating” effects. This phenomenon is dependent on the ability of a specific material (catalyst, solvent or reagent) to absorb microwave energy and convert it into heat. Microwave heating usually increases with the dielectric constant of the solvent, and in the presence of hydroxyl groups; thus the use of glycerol as reagent is particularly attractive for microwave activation. The short reaction time, and expanded reaction range that is offered by microwave-assisted syntheses are suited to the increased demands in chemical industry obtaining an interesting reactivity with peculiar selectivity. This method thus offers a

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practical alternative to conventional heating and traditional base catalysts. In addition, the use of solid catalysts in dry media is an additional benefit for no solvent is used, and there is no need for ultimate separation.

There are only a few studies about microwave-assisted glycerol reactions; Luque et al. reported the esterification of glycerol to polysaccharides and the oxidation of glycerol to glycolic acid and oxalic acid under microwave activation applying powers in the range 100–300 W for 30 min [13]. For the esterification of glycerol over H_2SO_4 , sulphated zirconia or Starbon®-400-SO3H catalysts, they reported 85–99 mol% glycerol conversion and of 60–75 mmol% selectivity to mono-, di- or tri-acetyl glycerol, depending on the reaction conditions. For the oxidation of glycerol over Pd-
Starbon®-400 catalysts, they reported glycerol 95 mol% conversions with glycolic acid selectivity up to 90 mol%. We report microwave-assisted dry-media liquid-phase direct reaction of glycerol with ammonia into acrylonitrile under microwave activation in the presence of solid catalyst; this process to acrylonitrile requires significantly milder conditions than those known in literature.

2. Experimental section

2.1. Catalyst preparation and characterization

The alumina-supported mixed Sb-V oxide catalysts were prepared using two methods, depending on the Sb precursor. In the first preparation method [14], Sb_2O_3 (Aldrich) was added to an aqueous solution of NH_4VO_3 (Sigma), this solution was kept under stirring at 80 °C for 50 min, then, $\gamma-Al_2O_3$ was added. The resulting solution was dried in a rotary evaporator at 80 °C and 0.3 atm. The resulting solid was dried at 115 °C for 24 h and then calcined at 400 °C for 4 h in air. For the second preparation method [14], the same procedure was used but Sb was added as soluble tartrate complex, prepared dissolving the required amount of antimony acetate (Aldrich) in tartaric acid (Sigma) 0.3 M. Both catalysts were prepared so that the total coverage of V + Sb would correspond to 100% of its dispersion limit on alumina; this dispersion limit is determined by Raman spectroscopy to be of ca. 9 atoms of Sb + V per nm^2 of alumina support [15,16]. The Sb/V atomic ratio was 1 and 3. For the sake of simplicity, the supported catalysts are labeled as $Sb_nV/Al_2O_3^*$ (where "n" indicates the atomic Sb/V ratio = 1 or 3) when the catalysts were prepared by the slurry method, and $Sb_nV/Al_2O_3^{**}$ (Sb/V = 1 or 3) when the catalysts were prepared by the tartrate method.

2.2. Reaction procedure

2.2.1. Conventional heat-induced reaction

A mixture of glycerol (0.5 mmol), hydrogen peroxide (15 mmol) and ammonia (57 mmol) was heated in a batch reactor at 100 °C while stirring and in the absence of any solvent. After five minutes, the catalyst (200 mg) was added and the reaction time started. The reactions were followed using a HP5890 gas chromatograph (GC) equipped with a 50 m long Ultra2-5% Phenyl methyl siloxane capillary column and a flame ionization detector (FID).

2.2.2. Microwave-activated reaction

The microwave equipment was a Multi-mode MicroSYNTH LabStation fitted with magnetic stirring and a PRO-6 Rotor reactor vessel. The temperature control during the reaction was carried out by an IR sensor. Milestone quartz vessels, with capacity of 5 mL, were used to carry out the microwave-activated reaction. These vessels use a pressure relief spring that vents the excess pressure only and reseals, with no loss of reagents. Glycerol (0.5 mmol) and 200 mg of the catalyst were blended in the quartz vessel and hydrogen peroxide (15 mmol) and ammonia (57 mmol) were added. The mixture was introduced in the microwave equipment and irradiated with a power high enough (0–100 W) to reach 100 °C of temperature with a heating ramp of 10 °C/min. The reactor vessel was held in the microwave for 1 h under continuous stirring. After cooling, the reaction products were extracted and filtered. The reaction was followed using a HP5890 gas chromatograph (GC) equipped with a 50 m long Ultra2-5% Phenyl methyl siloxane capillary column and a flame ionization detector (FID).

3. Results

3.1. Characterization of the catalysts

The catalysts have been characterized by Raman spectroscopy under dehydrated conditions (Fig. 1). In addition, the samples were characterized by XRD (not shown) and show no diffraction pattern but that of gamma-alumina; the absence of diffraction peaks belonging to bulk VO_x , SbO_x of Sb-V-O mixed phases, confirmed that the phases observed by Raman spectroscopy must be smaller than 4 nm.

Fig. 1A shows the Raman spectra under dehydrated conditions of reference vanadium oxide on alumina and antimony oxides on alumina, both at their dispersion limit loading. 1V/Al exhibits a Raman band near 1027 cm^{-1} , which is sensitive to hydration, characteristic dispersed surface vanadium oxide species [17]. 1Sb/

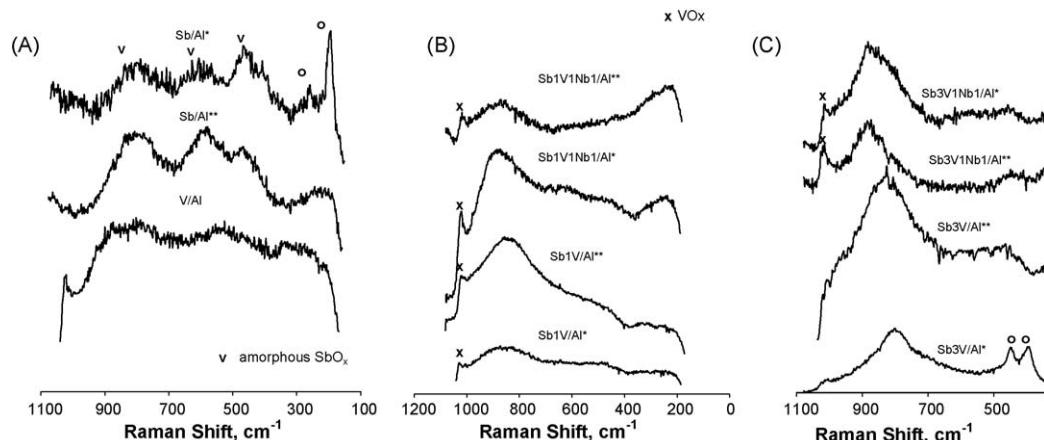


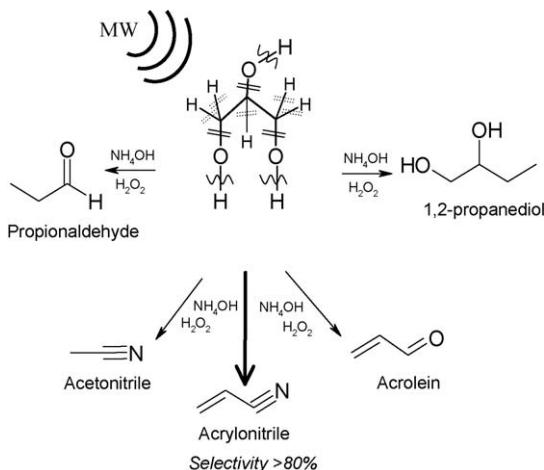
Fig. 1. Raman spectra under dehydrated conditions of: (A), reference V/Al, Sb/Al^* and Sb/Al^{**} ; (B), binary and ternary alumina-supported catalysts with Sb/V = 1 atomic ratio; (C), binary and ternary alumina-supported catalysts with Sb/V = 3 atomic ratio.

Al^{**}, prepared with the tartrate method, exhibits broad Raman bands near 780, 600, 468 and 210 cm⁻¹, which correspond to an amorphous antimony oxide overlayer, closely interacting with the alumina support [18]. 1Sb/Al^{*} exhibits the Raman bands of the amorphous antimony oxide overlayer on alumina and also new Raman bands at 190 and 255 cm⁻¹, which are the most intense of crystalline Sb₂O₃ aggregates [15]. Fig. 1B shows the Raman spectra of binary (Sb/V/Al) and ternary (Sb/VNb/Al) catalysts with Sb/V = 1 atomic ratio, whereas Fig. 1C shows their counterparts with an excess of antimony. At Sb/V = 1 atomic ratio (Fig. 1B), the spectra present a band near 1027 cm⁻¹, sensitive to hydration; characteristic of dispersed surface V(V) species [17]; in addition, a broad Raman band near 840–880 cm⁻¹ evidences the presence of alumina-distorted VSbO₄ phase [19]. While no different Raman bands are apparent upon change of preparation method, Sb₁V₁Nb₁/Al^{**} exhibits worse defined Raman bands. The addition of niobium shifts the broad band from 840–880 to 900 cm⁻¹, due to the contribution of V-Nb-O mixed phases [20]. With an excess of antimony, 1Sb₃V/Al^{*} exhibits essentially a Raman band near 800 cm⁻¹ of the rutile VSbO₄ phase resents and new Raman bands at 190, 255, 372 and 451 cm⁻¹, typical of α -Sb₂O₄ (Fig. 1C); segregated antimony oxides (Sb₂O₃ or α -Sb₂O₄) are not evident if the sample are prepared using the tartrate method or if niobium is present. Addition of niobium on either preparation method for 1Sb₃V₁Nb₁/Al shifts the Raman band of the rutile VSbO₄ phase from 840–880 cm⁻¹ to ca. 900 cm⁻¹, which evidences the incorporation of niobium into its lattice [21], the niobium ions may shift excess vanadium species, which disperse on alumina, as suggested by the Raman bands at 1027 cm⁻¹.

3.2. Catalytic activity

The reaction of glycerol to acrylonitrile also produces acrolein, 1,2-propanediol, propanal and acetonitrile (Scheme 1), which may decrease nitrile selectivity [7]. Fig. 2 shows the activity results obtained during glycerol to acrylonitrile reaction under conventional thermal activation. Acrylonitrile is obtained with high selectivity, although glycerol conversion is below 20%. Acrolein, propanal and propanediol are the main side products.

Fig. 3 shows a comparison of the catalytic data obtained under thermal and microwave activation methods. Under conventional thermal-activated reaction, the blank runs show negligible activity after 20 h at 100 °C. In the presence of a catalysts (alumina-supported Sb-V-O), thermal activation affords 13.9% glycerol conversion and 62.5% selectivity to acrylonitrile after 20 h at 100 °C. Blank microwave activation (100 °C) triggers glycerol



Scheme 1. Possible products in the catalytic reaction of glycerol with ammonia and hydrogen peroxide under microwave activation.

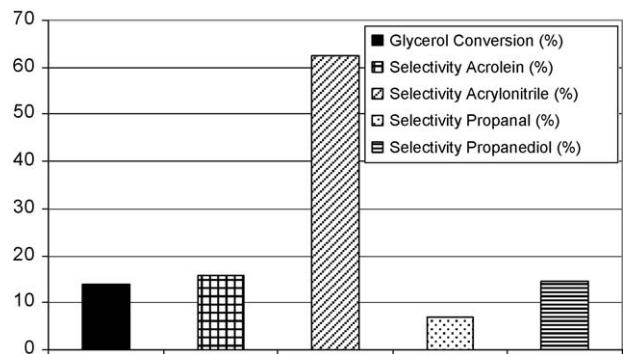


Fig. 2. Glycerol conversion (%) and selectivity (%) in the ammonoxidation of glycerol under conventional thermal activation (oil bath) at 373 K for 20 h for Sb₁V/Al^{**} catalyst. (**Slurry method Sb(CH₃COOH)₃ [tartric acid] and NH₄VO₃ [aq] + γ -Al₂O₃ powder: dried/calcined).

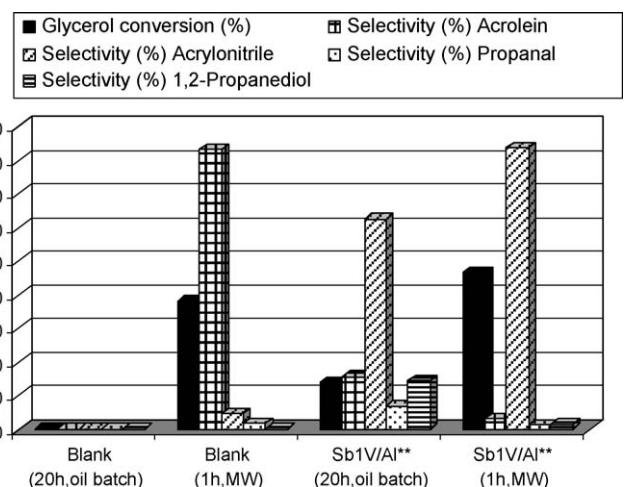


Fig. 3. Comparison of both activation methods: conventional thermal activation (20 h) and microwave activation (1 h), in the ammonoxidation of glycerol for acrylonitrile production. (**Slurry method Sb(CH₃COOH)₃ [tartric acid] and NH₄VO₃ [aq] + γ -Al₂O₃ powder: dried/calcined).

reactivity in 1 h affording rather high conversion (Fig. 3). In the absence of any catalyst, the MW activation dehydrates glycerol to acrolein (83% selectivity). In the presence of Sb₁V/Al^{**} catalyst, the conversion reaches 47% after 1 h under microwave activation (100 °C), and selectivity to acrylonitrile remarkably increases from 60 to 84%, compared to thermal activation, reaching a yield of 39.2% to acrylonitrile.

Table 1 illustrates the role of different catalysts for glycerol conversion to acrylonitrile under microwave activation. The selectivity to acrolein is quite high, near 83.3% in the absence of any catalyst. Acrolein remains as the main product on bare alumina, V/Al, Sb/Al^{*} and Nb/Al catalysts while minor amounts of acrylonitrile and propanal form. The antimony-containing catalyst performance depends on the antimony precursor, Sb/Al^{**} is essentially selective to 1,2-propanediol. The state of antimony species has an important effect on glycerol reactivity on the binary and ternary catalysts. V/Al produces acrylonitrile and acrolein. The presence of both antimony and vanadium affords catalysts highly efficient for glycerol conversion to acrylonitrile, affording almost 84% selectivity at 47% conversion in 1 h under microwave activation (100 °C). The presence of antimony triggers the ability of vanadium-containing catalysts to form the nitrile. The interaction between antimony and vanadium appears critical. Both stoichiometry and preparation method affect such interaction; an

Table 1

Yield (%) and selectivity (%) in the ammoxidation of glycerol for acrylonitrile production under microwave irradiation at 373 K, Power = 0–100 W, heating ramp = 10 °C/min, reaction time = 1 h.

Catalyst	Conv. (%)	Yield (%)	Selectivity (%)			
			Acrolein	Acrylonitrile	Propanal	1,2- Propanediol
Blank	38.2	1.8	83.3	4.7	1.9	–
Al_2O_3	36.4	5.1	56.0	14.0	13.9	6.3
Nb/Al	30.3	1.9	61.1	6.2	15.8	6.9
V/Al	33.3	10.1	48.1	30.5	11.4	
Sb/Al^*	20.5	2.8	47	13.9	5.0	24.1
Sb/Al^{**}	21.6	2.1	6.0	9.7	5.1	69.4
$\text{Sb}_1\text{V}/\text{Al}_2\text{O}_3^*$	20.1	8.7	40.3	43.4	5.3	–
$\text{Sb}_1\text{V}/\text{Al}_2\text{O}_3^{**}$	46.8	39.2	3.3	83.8	1.3	1.6
$\text{Sb}_3\text{V}/\text{Al}_2\text{O}_3^*$	12.0	7.3	17.4	60.7	12.5	9.4
$\text{Sb}_3\text{V}/\text{Al}_2\text{O}_3^{**}$	48.8	18.8	45.1	38.6	5.4	5.9
$\text{Sb}_1\text{V}_1\text{NV}/\text{Al}_2\text{O}_3^*$	21.4	4.1	44.7	19.3	6.4	19.5
$\text{Sb}_1\text{V}_1\text{Nb}_1/\text{Al}_2\text{O}_3^{**}$	56.0	8.3	20.2	14.8	1.8	49.2
$\text{Sb}_3\text{V}_1\text{Nb}_1/\text{Al}_2\text{O}_3^*$	51.1	2.4	72.7	4.7	1.6	7.2
$\text{Sb}_3\text{V}_1\text{Nb}_1/\text{Al}_2\text{O}_3^{**}$	14.5	1.2	13.9	8.2	5.9	62.5

Catalyst preparation:

*Slurry method (Sb_2O_3 and/or NH_4VO_3 [aq] + $\gamma\text{-Al}_2\text{O}_3$ powder: dried and calcined).

**Slurry method ($\text{Sb}(\text{CH}_3\text{COOH})_3$ [tartaric acid] and NH_4VO_3 [aq] + $\gamma\text{-Al}_2\text{O}_3$ powder: dried and calcined).

excess of antimony renders the system less efficient. At $\text{Sb}/\text{V} = 1$, the tartrate preparation method results in much more efficient catalyst; this is consistent with a more intimate entanglement between vanadium and antimony species, which agrees with the role of the rutile VSbO_4 phase.

Niobium doping of Sb-V-O based catalysts decreases the selectivity to acrylonitrile, this trend is particularly important for catalysts prepared with excess of antimony. It is interesting to underline that niobium doping on catalysts prepared by Sb_2O_3 slurry method shifts selectivity to acrolein, while for those prepared by the tartrate method shift selectivity to 1,2-propanediol. The molecularly dispersed antimony species in the tartrate method combine more extensively with vanadium and other components of the catalyst, which appear to result in more efficient performance to glycol. The Sb_2O_3 suspension preparation method for ternary V-Sb-Nb mixed oxides on alumina shifts product distribution to acrolein (which is the precursor to acrylonitrile); this is consistent with a less extensive formation of the rutile VSbO_4 .

4. Discussion

Microwave irradiation activates glycerol more efficiently than thermal activation; this results in dramatically milder reaction conditions demand (100 °C vs. ca. 400 °C) [7]. A remarkable feature is the ability of microwaves to activate glycerol, being acrolein the main reaction product in the absence of any catalyst. Acrolein appears to be a critical intermediate during the ammoxidation of C_3 hydrocarbons (propane and propylene) to produce acrylonitrile [22]. An interesting result is that microwave radiation, in the absence of a catalyst, may also activate ammonia to some extent, since small amounts of acrylonitrile are already detected. Microwave activation transforms glycerol into acrolein, which in the presence of an appropriate catalyst results in C–N bond formation. The results presented above show that different catalyst formulations produce acrolein, 1,2-propanediol or acrylonitrile in the microwave-activated reaction. Bare alumina and single oxides on alumina are not efficient catalysts for the glycerol to acrylonitrile reaction. The performance of supported binary catalysts strongly depends on composition, structure and preparation method.

The activity experiments show that the vanadium-containing catalysts are already selective to acrylonitrile formation (Table 1). When it is modified with antimony both VO_x and rutile VSbO_4 active sites are present and both conversion and selectivity to acrylonitrile increase. Thus, redox sites appear necessary to

introduce nitrogen into the glycerol molecule. It has been demonstrated that the interaction between antimony oxides and vanadium oxides may lead redox sites with enhanced catalytic activity that are able to transform acrolein intermediate into the desired acrylonitrile during propane ammoxidation [23]. If acrolein appears as a common intermediate in the formation of acrylonitrile from propane or from glycerol, it makes sense that the interplay between dispersed vanadium species and the rutile VSbO_4 phase accounts for the efficient formation of the nitrile.

The tartrate method molecularly disperses antimony and generates an amorphous layer of antimony oxide, which promotes the reaction between Sb and V into the rutile VSbO_4 phase, as confirmed by Raman bands in $1\text{Sb}_1\text{V}/\text{Al}^{**}$ sample (Fig. 1). The presence of redox sites with enhanced activity (VSbO_4) would explain the better performance detected for $\text{V}_1\text{Sb}/\text{Al}^{**}$ catalyst with respect V/Al and $\text{V}_1\text{Sb}/\text{Al}^*$ samples.

Small amounts of niobium modulate redox properties and increase acidity [24,25] rendering systems more efficient for selective oxidation and/or ammoxidation reactions. For many oxide systems, the promoting effect of niobium additive is limited to low loadings [26], and is typically lost when well defined niobium-containing phases (e.g., SbNbO_4) form [25,27]. SbNbO_4 is inactive for acrylonitrile formation during propane ammoxidation [21,28]. SbNbO_4 is a rather inert phase, while VSbO_4 rutile phase is highly dynamic, allowing for migration of antimony cations [29,30] due to the low energy barrier for antimony cations mobility [31], which facilitates the redox cycle between dispersed V^{5+} species on alumina and lattice V^{3+} species in the rutile VSbO_4 phase [30]. For glycerol to acrylonitrile reaction, niobium doping to alumina-supported V-Sb oxide catalysts is detrimental to acrylonitrile, shifting selectivity to acrolein or 1,2-propanediol. The results suggest that microwave activation may promote Nb–Sb interaction, thus poisoning catalyst performance.

5. Conclusions

Glycerol provides a renewable feedstock for a sustainable acrylonitrile process. We report an economical, solvent free, and efficient microwave-assisted synthesis of acrylonitrile, which may be a viable green alternative to present-time industrial process. Furthermore, microwave-activated reactions afford a significantly more active and selective process than thermal activation, which results in significantly milder reaction conditions. The main advantage of microwave activation is its ability to quickly convert

glycerol into acrolein, which is a reaction intermediate to acrylonitrile. An appropriate selection of catalyst formulation would afford high yield to acrylonitrile.

On the screened V-Sb-Nb oxides on alumina, ternary systems involving niobium are inefficient for the microwave-activated reaction of glycerol to acrylonitrile; binary, alumina-supported antimony-vanadium mixed oxide catalyst are efficient, being $\text{Sb}_1\text{V}/\text{Al}^{**}$ (prepared using the tartrate method) the most active and selective towards acrylonitrile under both conventional thermal and microwave activation procedures. The presence of the rutile VSbO_4 phase appears necessary to form the C–N bond. The microwave-assisted reaction of glycerol over this sample led to very satisfactory results, affording acrylonitrile selectivity close to 90% at conversion values near to 50%.

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